## PATENT ABSTRACTS OF JAPAN

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## (54) OPTICAL INFORMATION RECORDING MEDIUM

(57) Abstract:

PROBLEM TO BE SOLVED: To obtain a medium capable of recording and erasure repeated many times by forming a dielectric layer contg. at least lanthanum and boron. SOLUTION: This optical recording medium has at least a phase transition type optical recording layer and a dielectric layer on the substrate. A transparent resin such as polycarbonate or acrylic resin or glass may be used as the material of the substrate. A protective layer made of an optically transparent dielectric layer having a high m.p., a high softening point and a high decomposition temp., easy to form and having moderate heat conductivity is disposed in a prescribed thickness on the surface of the substrate. This dielectric layer contains at least lanthanum (La) and boron (B). Since LaB6 has great dependency of its absorption factor and extinction coefft. on wavelength, it is effective in controlling the absorption factor and reflectance of a multilayered film at the time of designing the thickness structure of the film by utilizing the interference effect of light.

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[Claim(s)]

[Claim 1] The medium for optical information record characterized by this dielectric layer containing (1) lanthanum and (2) boron at least in the medium for optical information record equipped with the phase transition type optical recording layer and the dielectric layer at least on the substrate.

[Claim 2] The medium for optical information record according to claim 1 characterized by the film density of a dielectric layer being 80% or more of theoretical density.
[Claim 3] The medium for optical information record according to claim 1 characterized by carrying out spatter membrane formation of the dielectric layer using the sputtering target which consisted of two or more elements which constitute this dielectric.
[Claim 4] The medium for optical information record according to claim 1 to 3 by which a dielectric layer is substantially characterized by the bird clapper from LaB6.

## [Translation done.] DETAILED DESCRIPTION

[Detailed Description of the Invention] [0001]

[The technical field to which invention belongs] this invention consists in the medium for optical information record which has a phase transition type optical recording layer. In detail, it is related with the medium for optical information record which has the phase transition type optical recording layer which reproduces [record, elimination, and ] information at high speed and with high density by irradiation of a laser beam etc. [0002]

[Description of the Prior Art] In recent years, the optical disk using the laser beam is developed as a record medium which meets expansion of amount of information, and the demand of the high density and improvement in the speed of record and reproduction. There are added type recordable only at once of a postscript and a rewritten type which any number of times can eliminate [record and] in an optical disk.

[0003] As a rewritten type optical disk, the magneto-optic-recording medium using the photoelectromagnetic effect and the phase-change medium using change of a reversible crystallized state are raised. A phase-change medium does not need an external magnetic field, but only modulates the power of a laser beam, and record and elimination are possible for it. Furthermore, it has the advantage that 1 beam over-writing which performs elimination and re-record simultaneously with a single beam is possible. [0004] The case where it eliminates by forming a record bit and making it crystallize by making record film make it amorphous by the phase-change recording method in which 1 beam over-writing is possible is common. As a record layer material used for such a phase-change recording method, a chalcogen system alloy thin film is used in many cases. For example, a germanium-Te system, a germanium-Te-Sb system, a In-Sb-Te system, a germanium-Sn-Te system alloy thin film, etc. are raised.

[0005] In addition, an added-a postscript type phase-change medium is also realizable with the almost same material and lamination as a rewritten type. In this case, it continues for a long period of time more in that there is no reversibility, information can be

recorded and saved, and theoretic almost semipermanent preservation is possible. Since the climax which is called rim around a bit unlike a perforation type does not arise when a phase-change medium is used as added type of a postscript, it excels in a signal quality, and there is an advantage that an opening does not need to make it an unnecessary hatchet air sandwich structure at the record layer upper part.

[0006] Generally, in a rewritten type phase-change record medium, in order to realize the crystallized state which is different from each other, two different laser light power is used. Elimination and the initial state crystallized with the amorphous bit in this method explain taking the case of the case where record and elimination are performed. Crystallization is higher than the crystallization temperature of a record layer enough, and is made by heating a record layer to temperature lower than the melting point. [0007] In this case, a record layer is pinched by the dielectric layer, or a cooling rate uses a long ellipse form beam in the move direction of a beam so that crystallization may become slow to sufficient grade carried out. On the other hand, amorphous-ization is performed by heating and quenching a record layer to temperature higher than the melting point. In this case, the above-mentioned dielectric layer also has a function as a heat dissipation layer for obtaining sufficient cooling rate (supercooling speed). [0008] Furthermore, in order to prevent the deformation accompanying melting and the volume change of the record layer in the above heating and cooling processes, and the thermal damage to a plastic plate or to prevent degradation of the record layer by moisture, the protective layer which consists of the above-mentioned dielectric layer is important. The quality of the material of protective-layer material is selected from viewpoints, such as having optically transparent being a thing, that the melting point, softening temperature, and a decomposition temperature are high, that formation is easy, and moderate thermal conductivity to a laser beam.

[0009] As a protective layer which has sufficient thermal resistance and a sufficient mechanical strength, dielectric thin films, such as a metaled oxide and a nitride, are raised first. Since coefficient of thermal expansion differs from an elastic property greatly, while these dielectric thin films and plastic plates repeat record and elimination, they become the cause which peels from a substrate and produces a pinhole and a crack.

[0010] Moreover, although a plastic plate tends to produce curvature with humidity, peeling of a protective coat may arise also by this. On the other hand, as a new dielectric protective layer, ZnS is made into a principal component and the thing in which SiO2 and the Y2O3 grade were made to mix is proposed. These conjugated compound protective coats are excellent in the adhesion to chalcogenide type alloy thin films, such as GeTeSb often used as a record layer, compared with the pure oxide or the nitride dielectric film. For this reason, in addition to the endurance over repeat over-writing, the film exfoliation in an accelerated test is raising the reliability of a phase-change medium further few. [0011]

[Problem(s) to be Solved by the Invention] However, a conjugated compound does not necessarily demonstrate a property to only mix. Reliability may be reduced on the contrary rather than the case where each pure compound is used depending on the composition range and the physical properties of a bipolar membrane. [0012] Although much proposals were conventionally made about the protective coat which is a compound containing a chalcogenide type element and which made ZnS, ZnSe, etc. mix an oxide, a nitride, a fluoride, carbide, etc., it set in part and was only

indicating the optimal composition range, and even if it used the mixture of the composition, the property superior to the protective layer which consists of the original pure compound simple substance was not necessarily acquired.

[0013] Since the compound from which, as for this, the physical properties of the above-mentioned composite constitute it is large and it differs, the physical-properties change by the manufacturing method and others is because \*\*\*\*\*\*\*\*\*. For example, although the spatter is widely used in forming the protective layer which consists of the above-mentioned conjugated compound, the physical properties of the conjugated compound protective coat naturally obtained differ by the case where a composite target is used, and the case where a simultaneous spatter is carried out using each compound target.

[0014] Moreover, it is a well-known fact that physical properties change with the pressures at the time of a spatter etc. also by the same manufacturing method. It was a technical problem how while dispersion in such protective coat physical properties exists, the protective coat suitable for the phase-change medium is found out.

[0015]

[Means for Solving the Problem] The medium for optical information record of this invention consists in the medium for optical information record characterized by this dielectric layer containing (1) lanthanum and (2) boron at least in the medium for optical information record equipped with the phase transition type optical recording layer and the dielectric layer at least on the substrate.

[0016]

[Embodiments of the Invention] The composition of the medium for optical record by this invention is described. The medium for optical record of this invention is equipped with the phase transition type optical recording layer and the dielectric layer at least on the substrate. Usually, it has the composition of a substrate / dielectric layer / record layer / dielectric layer / reflecting layer.

[0017] Transparent resins, such as a polycarbonate, an acrylic, and a polyolefine, or glass can be used for a substrate. The dielectric layer which fulfills the above-mentioned property is usually prepared in a substrate front face at the thickness of 10 to 500nm. The deformation prevention effect of a substrate or record film is inadequate in the thickness of a dielectric layer being less than 10nm, and there is an inclination not to make the duty as a protective layer.

[0018] If it exceeds 500nm, the difference of the internal stress of the dielectric layer itself or elasticity with a substrate will become remarkable, and it will become easy to generate a crack. A dielectric layer contains a lanthanum (La) and boron (B) at least. Since it has a wavelength dependency with big absorption coefficient and extinction coefficient, especially LaB6 is effective in the absorption and control of a reflection factor, when designing the thickness composition of a multilayer using the interference effect of light.

[0019] this invention is not limited to the two above-mentioned element. A principal component, then other dielectrics may be mixed in La and boron. As other dielectrics, SiO2, Y2O3, ZrO2 and BaO, B-2s Ta [O3 and ]2O5, NdF3 and ZnS, Si3N4, SiC, etc. are mentioned. When mixing other dielectrics in a dielectric, it has the thermal resistance of 1000 degrees C or more, and an optically transparent thing is desirable.

[0020] As for the above-mentioned dielectric layer, it is desirable to prepare using the compound sputtering target which consisted of two or more elements which constitute

this dielectric. Although the spatter is usually widely used in case this forms the dielectric layer which consists of the above-mentioned matter, since the homogeneity of the composition element of the compound protective coat obtained won compared with the direction which uses a compound target carrying out a simultaneous spatter using each simple substance target, it is because it becomes what was excellent also in the property as a protective coat.

[0021] As for the above-mentioned dielectric layer, it is desirable that film density is 80% or more of theoretical density. Here, although membranous theoretical density was shown by the following formula and multiplied the density in the bulk state of each composition compound by the mol content of the composition compound, it is integrated value. Theoretical density = sigma {(density of a composition compound bulk state )x (composition compound mol content)}

By carrying out density of a mixture dielectric layer in this way, the endurance over repeat record and aging can be raised remarkably.

[0022] It is good to make a degree of vacuum low (for it to be low about argon gas pressure) for making high film density which can be performed by adjusting the degree of vacuum at the time of sputtering in controlling film density, and it is good to usually set preferably 1Pa or less of degree of vacuums to about 0.8-0.1Pa. moreover, Ar gas usually preferably used in spatter electric discharge -- the oxygen of a minute amount -- or you may mix nitrogen gas again

[0023] The record layer of the medium of this invention is a phase-change type record layer, and the thickness has the desirable range of 10 to 100nm. Sufficient contrast will be hard to be acquired if the thickness of a record layer is thinner than 10nm. Moreover, there is an inclination for crystallization speed to become slow and record elimination in a short time becomes difficult. Since it will be hard coming to obtain too optical contrast and will become easy to produce a crack on the other hand if 100nm is exceeded, it is not desirable.

[0024] In addition, the thickness of a record layer and a dielectric layer also takes into consideration the interference effect accompanying multilayer composition, its absorption efficiency of a laser beam is good, and it is chosen so that the amplitude of a record signal, i.e., the contrast in a record state and the state where it does not record, may become large. It is chosen as a material [ over-write / 3 yuan compounds, such as GeSbTe or InSbTe, / as a record layer / material ].

[0025] It is also effective to add a kind or the element beyond it and to improve crystallization speed, an optical constant, and oxidation resistance from from to these 3 yuan compounds, among Sn, In, Pb, As, Se, Si, Bi, Au, Ti, Cu, Ag, Pt(s), Pd, Co(es), nickel, etc. of 0.1 - 10 atom %. Although the optical reflecting layer and the hard-coat layer for heat deformation prevention are prepared on the protective layer, an optical reflecting layer has the desirable matter with a large reflection factor, and Au, Ag, Cu, aluminum, etc. are used.

[0026] for a certain reason, a small amount, in addition \*\* of the effect which promotes diffusion of the heat energy which the record layer absorbed are [ this reflecting layer ] good in Ta, Ti, Cr, Mo, Mg, V, Nb, Zr, etc. because of thermal conductivity control etc. A record layer, a dielectric layer, and a reflecting layer are formed by the sputtering method etc. It is desirable at the target for record film, the target for protective coats, and the point that performing film formation with the in-line equipment which installed the

target for reflecting layer material in the same vacuum chamber when required prevents the oxidization and contamination between each class. Moreover, it excels also from the field of productivity.

[0027]

[Example] Although this invention is explained in detail with an example below, this invention is not limited to the following examples, unless the summary is exceeded. Using the sintered-compact target which obtained LaB6 powder in hot pressing as an example 1 dielectric-layer material, the dielectric layer / record layer / dielectric layer / reflecting layer was prepared on the polycarbonate resin substrate, and the record medium of four layer structures was created. Thickness of each class was made into 180nm of lower dielectric layers, 30nm of record layers, 30nm of up dielectric layers, and 100nm of reflecting layers.

[0028] Composition of a record layer is germanium22.2Sb22.2Te55.6. The reflecting layer used the aluminum-Ta alloy. The dielectric layer formed membranes by RF (13.56MHz) sputtering by Ar gas pressure of 0.7Pa, and oxygen-gas-pressure force 15mPa. Film density was 4.1g/cc, and was 87% of theoretical density. The record layer and the reflecting layer formed membranes by DC sputtering with Ar gas pressure of 0.7Pa. Furthermore, ultraviolet-rays hardening resin with a thickness of about 4 micrometers was prepared.

[0029] After performing initialization, i.e., crystallization processing of a record layer, for this disk using Ar ion laser, the following conditions estimated the dynamic characteristics of a disk. Whenever repeatedly and it reached the predetermined number of times, making it rotate with the linear velocity of 10 m/s, measurement of C/N ratio and an elimination ratio was performed. [ using 4MHz and duty 50% pulsed light ] [ record power 16.5mW and base power 9mW ] As a result was shown in drawing 1, as compared with the 1st time, the fall of C/N was about 2dB repeatedly in 1000 repeats, and the elimination ratio was repeatedly equivalent to the 1st time also in 10,000 times. [0030] Except having set the fine particles of ZnS and TiO2 to 80 to 20 by the mol ratio as a dielectric-layer material in example of comparison 1 example, the disk was created similarly and same dynamic characteristics evaluation was performed. The result was shown in drawing 2. As compared with the 1st time, the fall of C/N is about 12dB repeatedly in 2000 repeats, and the elimination ratio fell by about 15dB in 2000 times as compared with the 1st time repeatedly so that clearly from the graph of drawing 2.

[Effect of the Invention] many [ to utilization of the medium in which this kind of repeat record and elimination are possible / by using the medium for optical record of this invention / many repeat record and elimination can be performed, and ] -- it is alike and effective

[Translation done.]



